

Conversion of metam sodium and emission of fumigant from soil columns

Wei Zheng^{a,b,*}, Scott R. Yates^b, Sharon K. Papiernik^c, Joe Nunez^d

^a*Department of Environmental Sciences, University of California, Riverside, CA 92521, USA*

^b*USDA-ARS, Soil Physics and Pesticides Research Unit, George E. Brown Jr Salinity Laboratory, Riverside, CA 92507, USA*

^c*USDA-ARS, North Central Soil Conservation Research Laboratory, 803 Iowa Ave., Morris, MN 56267, USA*

^d*University of California Cooperative Extension Farm and Home, 1031 South Mt. Vernon Ave., Bakersfield, CA 93307, USA*

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Abstract

Metam sodium is the most widely used soil fumigant in the United States. The primary breakdown product of metam sodium in soil is methyl isothiocyanate (MITC), an active pesticidal agent with a high toxicity and a great potential for volatilization. Reducing atmospheric emissions of MITC is therefore critical to maintain air quality. The objective of this study was to examine the rate and efficiency of conversion of metam sodium to MITC in soil and to investigate the potential of using surface water sealing to reduce MITC emissions. The conversion of metam sodium to MITC was a rapid abiotic decomposition process. At typical field application rates, the conversion efficiency depended on the initial content of metam sodium in soil, but was independent of soil moisture, soil type, and soil atmospheric conditions. A soil column system was used to measure the emission and distribution of MITC after subsurface and surface application of metam sodium. Volatilization flux and cumulative emission loss of MITC was substantially reduced with surface water sealing compared to uncovered soil columns after subsurface application of metam sodium. When metam sodium was surface applied in simulated chemigation, surface water sealing was ineffective, suggesting the need for additional emissions reduction practices when metam sodium is broadcast. Overall, the results of the column experiment indicate that surface water sealing with subsurface application of metam sodium may be an effective and economical strategy to reduce MITC emissions while maintaining pest control efficacy.

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1. Introduction

Fumigants have been used extensively for decades to control soil-borne pests before the planting of a variety of fruits and vegetables. Metam sodium, a member of the dithiocarbamate chemical family, is the first most heavily used fumigant in the United States with agricultural use of 57–62 million pounds per year (Kiely et al., 2004). It is likely that use of

Abbreviations: MITC, methyl isothiocyanate; GC, gas chromatography; NPD, nitrogen–phosphorus detector

*Corresponding author. George E. Brown Jr., Salinity Laboratory, 450 W. Big Springs Road, Riverside, CA 92507, USA. Tel.: +1 951 369 4878; fax: +1 951 342 4964.

E-mail address: wzheng@ussl.ars.usda.gov (W. Zheng).

metam sodium in agriculture will increase with the worldwide phase-out of methyl bromide. Metam sodium decomposes rapidly to methyl isothiocyanate (MITC) in soil, which provides the primary biocidal activity (Wales, 2000). Methyl isothiocyanate is more toxic than metam sodium with mouse intraperitoneal LD₅₀ values of 100 and 750 mg kg⁻¹, respectively (Lam et al., 1993).

Previous investigations pertaining to the environmental fate of metam sodium and MITC have been conducted in an effort to improve pest control efficacy and to avoid crop injury associated with persistent fumigant residues (Wales, 2000; Zheng et al., 2004). The conversion rate of metam sodium to MITC is very rapid in soil, usually completed within 1 h to 1 day following application (Gerstl et al., 1977; Wales, 2000). The rate of decomposition depends strongly on soil temperature, soil texture, and soil moisture. The efficiency of conversion in soil is reported to be very high, ranging from 87% to 95% (Turner and Corden, 1963; Smelt et al., 1989; Wales, 2000), but most of these studies investigated high metam sodium application rates (Turner and Corden, 1963; Smelt and Leistra, 1974; Gerstl et al., 1977). Less emphasis has been given to the conversion of metam sodium at application rates representative of typical contemporary fumigant usage in fields.

Compared to the non-volatile metam sodium, MITC has a relatively high vapor pressure (16.0 mmHg at 20 °C), which allows it to volatilize and disperse in the gas phase. Therefore, the primary environmental concern associated with metam sodium agricultural applications is the substantial emissions of MITC to the atmosphere. It has been reported that as much as 10–60% of the applied metam sodium may be lost via MITC volatilization from field or greenhouse soil (Leistra and Crum, 1990; Van den Berg, 1992; Van den Berg et al., 1999). The emission loss of MITC depends on various factors such as application technique, climatic conditions, soil temperature, soil moisture, and soil texture characteristics. The application rate of metam sodium (over several hundreds pounds per acre) is two orders of magnitude greater than that of most conventional pesticides. The high application rates and high mammalian toxicity of MITC indicate that large emissions of this fumigant into the atmosphere has the potential to endanger farm workers and others living and working near fumigated fields. Hence, developing strategies to minimize emissions is imperative.

Generally, MITC emissions can be reduced by increasing fumigant degradation in soil, which may be achieved by enhancing the MITC degradation rate or by increasing the fumigant residence time in soil using physical containment (diffusion barriers). Increasing the capacity of soil to degrade MITC by abiotic and biotic mechanisms has been demonstrated by applying organic amendments (e.g. manure) at the soil surface, which substantially reduced volatilization losses (Gan et al., 1998; Dungan et al., 2003). Fumigation strategies that increase the fumigant residence time in soil are currently the most common and feasible approaches to reduce fumigant emissions. These include tarping with a film (plastic, paper or fabric), applying a water seal by irrigation, and increasing the depth of fumigation and the bulk density of the soil (Yates et al., 2002). Among physical containment approaches, surface water sealing is an economical and promising strategy to reduce fumigant emissions. Initial or intermittent surface water sealing has shown great potential to improve field retention of MITC and reduce off-gassing rates of MITC from metam-sodium applications (Sullivan et al., 2004). Increasing the surface soil water content may reduce the soil air-filled pore space and thereby restrict fumigant diffusion into air (Jin and Jury, 1995; Yates et al., 2002).

The primary objectives of this study were to investigate the conversion of metam sodium to MITC at field application rates, to determine the effect of various factors on the transformation process, to quantify the volatilization of MITC from soil after metam sodium application, and to evaluate the potential of surface water sealing in reducing MITC emissions. Emissions of MITC were assessed using a soil column system, which has been successfully used to monitor the emission and distribution of fumigants and to screen new fumigation strategies prior to field evaluation (Gan et al., 2000). This study aims to comprehensively investigate the environmental fate of metam sodium following its application to soil, including MITC formation, volatilization, and emission reduction with surface water sealing.

2. Materials and methods

2.1. Chemicals and soils

Metam sodium (dihydrate, purity 99%) was purchased from Chem Service (West Chester, PA).

Methyl isothiocyanate standard (purity 99%) was obtained from Sigma Chemical Co. (St. Louis, MO). Vapam (420 g kg^{-1} metam sodium) was provided by Amvac Chemical Co (Newport Beach, CA). All chemicals were used as received.

The soil used in the column study and most incubation experiments was an Arlington sandy loam soil (coarse-loamy, mixed, thermic Haplic Durixeralf) collected from the University of California Agricultural Experiment Station in Riverside, CA. Other soils used in the incubation study were Hanford sand (coarse-loamy, mixed, superactive, non-acid, thermic Typic Xerorthents; Fresno, CA), Imperial silty clay (fine, smectitic, calcareous, hyperthermic Vertic Torrifluvents; Imperial, CA), Sesame sandy loam (fine-loamy, mixed, thermic Typic Haploxerolls; Paso Robles, CA), Linne clay loam (fine-loamy, mixed, superactive, thermic Calcic Pachic Haploxerolls; Paso Robles, CA), and Webster clay loam (fine-loamy, mixed, mesic Typic Endoaquoll; Lamberton, MN). The soils had not been previously treated with any fumigant. All soils were passed through a 2.0-mm screen without air-drying and stored at low temperature (4°C) before use. Selected physical and chemical properties of the soils are given in Table 1. For experiments evaluating the impact of biological degradation on the formation and persistence of MITC in soil, Arlington sandy loam soil was autoclaved twice at 121°C for 1 h with a 1-d interval between the first and second autoclaving.

2.2. Batch incubation experiments

The rapid formation of MITC from metam sodium was determined in soil by measuring the gas concentration of MITC in sealed headspace

vials. Ten grams (dry weight equivalent) of soil was weighed into 20-mL headspace vials. Soil moisture was adjusted by adding distilled water or by air-drying. Aqueous stock solution ($500 \mu\text{L}$) of fumigant (metam sodium or MITC) was injected into each sample vial. All treated vials were immediately capped with an aluminum seal and Teflon-faced butyl rubber septa and then were incubated at $21 \pm 0.5^\circ\text{C}$ in darkness. At regular intervals, fumigated samples were sacrificed from the incubator to analyze the air concentration of MITC within the vial headspace. Gas samples ($500 \mu\text{L}$) were withdrawn by piercing the rubber serum cap with a gas-tight syringe. The gas samples were immediately transferred into 10-mL headspace vials and capped. All treatments were replicated three times.

To assess the conversion efficiency of metam sodium in soil, the concentration of MITC in the sample vials was determined based on soil extracts of the fumigant (Zheng et al., 2004). Briefly, after 1 h incubation, triplicate soil samples were removed from the incubator ($21 \pm 0.5^\circ\text{C}$) and frozen at -21°C . Preliminary experiments showed that the transformation of metam sodium to MITC was complete within 0.5 h for soil samples in this experiment. To ensure complete conversion of metam sodium into MITC in soil, 1 h of incubation time was allowed prior to measuring the conversion efficiency of metam sodium. Fumigant MITC was extracted from soils by adding anhydrous sodium sulfate (8 g) and ethyl acetate (10 mL) to sample vials while they were still frozen, sealing the vials immediately, vigorously shaking for 1 h, and vortexing for 2 min at room temperature. A portion of the ethyl acetate extract was transferred to a gas chromatography (GC) vial and analyzed by GC. Soil samples treated directly with MITC were

Table 1
Conversion efficiency of metam sodium (0.5 mmol kg^{-1}) to MITC in different soils and different atmospheric conditions^a

Soil	Clay (%)	Sand (%)	Silt (%)	OC (%)	pH	Conversion efficiency (%)
Hanford sand	3.6	95.6	0.8	0.33	7.5	94.3 ± 2.8
Imperial silty clay	42.5	10.8	46.7	1.12	7.1	98.2 ± 1.9
Sesame sandy loam	11.8	67.5	20.7	1.42	5.7	92.8 ± 0.2
Linne clay loam	31.3	36.7	32.0	2.51	6.8	95.1 ± 1.1
Webster clay loam	28.8	35.4	35.8	3.48	5.2	92.6 ± 2.4
Arlington sandy loam	7.4	74.6	18.0	0.92	7.2	$95.0 \pm 0.3 \text{ a}$
Control						$95.7 \pm 0.9 \text{ a}$
Air						$95.7 \pm 0.9 \text{ a}$
N ₂						$94.1 \pm 0.5 \text{ a}$

^aValues for each conversion efficiency of metam sodium in each experiment followed by different letters are significantly different ($\alpha = 0.05$) by Tukey's mean separation test.

extracted and analyzed in the same way. Preliminary experiments indicated that the recovery of MITC from soil was >95% using the above procedures.

To investigate the effect of various factors on the conversion of metam sodium to MITC, a series of incubation experiments was conducted: (1) autoclaved and non-sterile Arlington sandy loam at 9.5% (w/w) soil moisture treated with metam sodium and MITC at 0.5 mmol kg^{-1} ; (2) Arlington sandy loam at soil water contents of 5%, 10%, 20% and 30% (w/w) treated with metam sodium at 0.5 mmol kg^{-1} ; (3) Arlington sandy loam (10% soil moisture) treated with metam sodium at 0.5, 2.5, 10, 20, and 40 mmol kg^{-1} ; (4) six soils (soil moisture approximately 60% of soil maximum water holding capacity) treated with metam sodium at 0.5 mmol kg^{-1} ; and (5) Arlington sandy loam (10% moisture) treated with metam sodium at 0.5 mmol kg^{-1} with initially anaerobic and aerobic soil atmospheres, in which vials containing soil were purged for 30 min with air (aerobic) or nitrogen (anaerobic) before fumigation. In all cases, incubation experiments were conducted at room temperature ($21 \pm 0.5^\circ\text{C}$). The conversion efficiency of metam sodium to MITC in different treatments was subjected to statistical analyses using a multivariate analysis-of-variance test.

2.3. GC analysis

The concentration of MITC in gas samples was determined using a Hewlett-Packard (HP) 6890 GC equipped with an automated headspace sampler. The operating conditions of the headspace sampler were: 80°C oven temperature, 90°C loop temperature, 100°C transfer line temperature, 5-min vial equilibration time, and 0.2-mL sample loop. For GC, a 30 m DB-VRX, $0.25 \text{ mm i.d.} \times 1.4 \mu\text{m}$ film thickness fused-silica capillary column (J&W Scientific, Folsom, CA) in conjunction with a nitrogen-phosphorus detector (NPD) was used. The chromatographic conditions were 1.5 mL min^{-1} carrier gas flow rate (He), 240°C inlet temperature, 280°C detector temperature, and 100°C isothermal oven temperature. The retention time for MITC was 5.1 min.

Ethyl acetate extracts of soil samples were analyzed for MITC using an HP 6890 GC equipped with an on-column injector. Similar GC conditions were used to determine MITC in solvent extracts except that the initial oven temperature was 50°C

for 1 min and the temperature was increased to 80°C at $4.0^\circ\text{C min}^{-1}$, then increased to 120°C at $30^\circ\text{C min}^{-1}$, and finally held for 2 min. Under these conditions, the retention time of MITC was 7.9 min.

2.4. Column experiments

The column system utilized in these studies was described in detail by Gan et al. (1996, 2000). Briefly, stainless steel columns (70 cm with 12 cm i.d.) were uniformly packed with fresh Arlington sandy loam at a bulk density of 1.50 g cm^{-3} and moisture of $\sim 5.0\%$ (w/w). To collect soil gas samples, gas-tight syringes were used to withdraw 0.1 mL aliquots of soil air from sampling ports located at 2, 5, 10, 20, 30, 40, 50, 60, and 70 cm below the soil surface. A Teflon tube attached to the inside of each sampling port was extended to the center of the column. All soil gas samples were immediately transferred to 10-mL headspace vials and analyzed by GC using the method described above. To monitor fumigant volatilization, a sampling chamber (4 cm with 12 cm i.d.) with an inlet and an outlet was sealed onto the top of soil column. A continuous and constant air flow (100 mL min^{-1}) was passed through the sampling chamber to sweep fumigant vapor escaping from the soil surface into the headspace inlet of GC, which was directly connected the outlet of the sampling chamber. Once metam sodium was injected into the column, the volatilization flux from each column was automatically monitored at 42-min intervals using a computerized relay system in tandem with an Agilent Technology 6890N Network GC. The soil column experiments were conducted at laboratory room temperature ($21 \pm 0.5^\circ\text{C}$).

The cumulative volatilization loss of MITC was calculated by integrating the instantaneous volatilization fluxes over time for the entire experiment (13 d). Instantaneous volatilization fluxes were calculated as $\text{mg min}^{-1} \text{ m}^{-2}$ and cumulative emission losses as a percentage of total applied fumigant (assuming 100% conversion of metam sodium). The GC conditions used for on-line monitoring were as follows: 100- μL gas sampling loop; 60 m DB-624, $0.25 \text{ mm i.d.} \times 1.4 \mu\text{m}$ film thickness fused-silica capillary column (J&W, Folsom, CA); 1.6 mL min^{-1} carrier gas flow rate (He); 100°C isothermal oven temperature; 220°C inlet temperature; and 290°C detector (NPD) temperature. Under these conditions, the retention time of MITC was 7.5 min.

To investigate the emissions of MITC and to evaluate the potential of using surface water sealing to reduce MITC emissions, four treatments were included in the column experiments: (1) 500 μL of MITC stock solution ($\sim 154\text{ mg}$ in acetone), which corresponds to the recommended field application rate (250 kg ha^{-1}), was injected into the column center at 20 cm depth (no surface treatment); (2) 530 μL of Vapam (equivalent to 154 mg of MITC obtainable from metam sodium at 100% conversion) was injected at the center of the column at 20 cm below the soil surface without any surface treatment; (3) 150 mL of water was sprayed on the soil surface just before the metam sodium (530 μL of Vapam) was injected into the soil column at 20 cm depth; and (4) 530 μL of Vapam was dissolved into 50 mL of water and delivered to the soil column surface, immediately followed by spraying 100 mL of water. Duplicate columns were used for each treatment to quantify system variability.

3. Results and discussion

3.1. The conversion of metam sodium and degradation of MITC

Metam sodium is applied as a soil fumigant in a stabilized aqueous solution (e.g. Vapam, 42% metam sodium). Upon contact with moist soil, metam sodium breaks down rapidly into two initial products, MITC and bisulfide (Zheng et al., 2004):



The bisulfide may further undergo a precipitation reaction with many metal ions (e.g. iron, copper, and manganese) existing in soil, or transform to elemental sulfur via an oxidation process, or be released into air as hydrogen sulfide (H_2S). These further transformations facilitate the conversion of metam sodium to MITC. A previous report indicated that traces of iron and copper salts in aqueous solution could contribute to this conversion (Ashley and Leigh, 1963).

The formation and degradation of MITC are shown in Fig. 1 where metam sodium (0.5 mmol kg^{-1}) was applied to non-sterile and autoclaved Arlington sandy loam at 9.5% soil moisture. This initial concentration corresponds to the recommended field application rate of metam sodium (250 kg of active ingredient per hectare), assuming a uniform distribution in the top 30 cm of soil (1.50 g cm^{-3} soil bulk density). No significant increase in headspace MITC

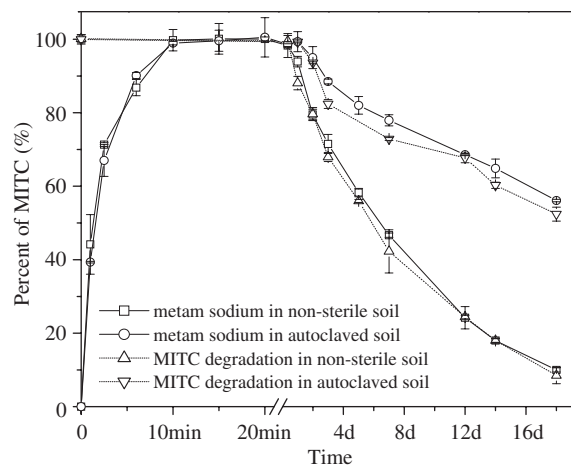


Fig. 1. Conversion of metam sodium (0.5 mmol kg^{-1}) and degradation of MITC in non-sterile and autoclaved Arlington sandy loam at 9.5% (w/w) soil moisture and 21°C . Note that formation of the MITC from metam sodium was observed by determining the gas concentration of MITC in headspace vials. The degradation of MITC was determined by measuring the concentrations of MITC in soil samples. The highest detected concentrations of MITC in the headspace or soil of vials were treated as 100%. Data points are the mean of triplicate samples; error bars indicate the standard error.

concentrations occurred at times $> 10\text{ min}$ after metam sodium addition to both non-sterile and autoclaved soils (Fig. 1), which suggests that the immediate formation of MITC is primarily attributed to a rapid abiotic decomposition of metam sodium and that soil microbial activity might have little impact on the conversion. However, the degradation of MITC in non-sterile and autoclaved soils was distinctly different. The dissipation of MITC in non-sterile soil is much faster than in autoclaved soil (Fig. 1), suggesting that soil microorganisms play an important role in MITC degradation. This is in agreement with previous observations (Dungan et al., 2003; Gan et al., 1998, 1999).

A similar experiment was conducted in which MITC (0.5 mmol kg^{-1}) was applied directly to non-sterile and autoclaved soils. Dissipation was similar to that observed for MITC derived from the conversion of metam sodium (Fig. 1). The extremely rapid conversion of metam sodium did not influence the degradation rate of MITC in soil. Overall, the conversion of metam sodium to MITC in soil is an abiotic decomposition process, which is complete in a very short time. The further degradation of MITC in non-sterile soil is controlled by biotic and abiotic mechanisms.

3.2. Effect of soil moisture on the conversion of metam sodium

The formation of MITC from metam sodium in Arlington sandy loam with different soil moistures is depicted in Fig. 2. Although the conversion of metam sodium to MITC was appreciably delayed with increasing soil moisture, the entire transformation process was still accomplished in a short time at all soil moistures. For example, the maximum concentrations of MITC in the headspace of vials were reached in 10 min in soil at 5% and 10% moisture content, suggesting that a complete conversion of metam sodium occurred within this short time. The maximum amount of MITC was obtained in approximately 20 min in soil at 20% moisture. In the saturated soil (30%), metam sodium completely disappeared in about 0.5 h. In this study, the conversion of metam sodium to MITC was significantly faster than previously reported for high application rates of metam sodium (a few hours to a day) (Turner and Corden, 1963; Smelt and Leistra, 1974), but was similar to observations in which a concentration of metam sodium ($48 \mu\text{g g}^{-1}$ soil) corresponding to a field application rate was used (Gerstl et al., 1977).

In addition to the effect of soil moisture on the formation rate of MITC, soil water content affects volatilization of MITC as shown in Fig. 2. High air concentrations of MITC were released from soil with a low water content, which suggests that increasing soil water content is a means of reducing

fumigant emissions. For instance, the maximum air concentration of MITC observed in sealed vials containing soil at 5% moisture is approximately 3-fold higher than the maximum MITC concentration in the headspace of vials containing soil at 30% moisture (Fig. 2). A moist soil layer or ponded water has been observed to reduce MITC emissions (Wang et al., 1997; Sullivan et al., 2004) because of the reduced diffusion of MITC resulting from the reduction in the soil's air-filled pore space and the increased partitioning of MITC out of the gas phase.

The conversion efficiency of metam sodium to MITC in soils at different moisture contents is summarized in Table 2 based on fumigant soil extracts. Results clearly show that the conversion efficiency of metam sodium to MITC is very high ($>92\%$) at all soil water contents, and soil moisture is expected to have no impact on the conversion efficiency of metam sodium. These results indicate that increasing the water content at the soil surface to reduce MITC emissions should not adversely impact the production of MITC from metam sodium.

3.3. Effect of metam sodium application rate on its conversion

The evolution profile of MITC, the initial product of metam sodium decomposition, is inversely proportional to loss of metam sodium. The formation of MITC was well described by a single exponential function as follows:

$$C = a(1 - e^{-kt}), \quad (1)$$

where C represents the concentration of MITC, a is the initial concentration of metam sodium in soil, k is the pseudo-first-order rate constant, and t is the time. The formation rate constant (k) of MITC was obtained from nonlinear least-squares fit of the experimental data to Eq. (1).

Values of k for MITC measured for a variety of metam sodium application rates are shown in Table 3. The formation rate (k) of MITC decreased with increasing metam sodium application rate in soil. For example, the formation half-life of MITC decreased by approximately a factor of 4 when the application rate of metam sodium increased from 0.5 to 40 mmol kg^{-1} (Table 3). These results indicate that the rate of metam sodium conversion to MITC in soil depends on the initial concentration of metam sodium.

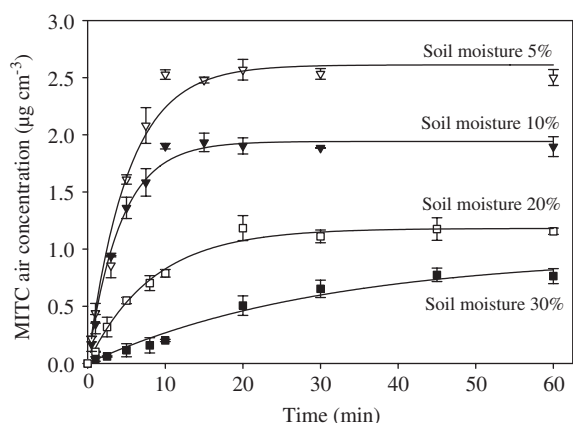


Fig. 2. The effect of soil moisture on the formation and volatilization of MITC produced from the decomposition of metam sodium (0.5 mmol kg^{-1}) in Arlington sandy loam at 21°C . Data points are the mean of triplicate samples; error bars indicate the standard error.

Table 2

Conversion efficiency of metam sodium to MITC in Arlington sandy loam with different soil moisture contents and different initial application rates of metam sodium

Soil moisture (w/w); metam sodium applied at 0.5 mmol kg ⁻¹	Conversion efficiency (%) ^a	Application rate of metam sodium (mmol kg ⁻¹); soil moisture at 10%	Conversion efficiency (%) ^a
5%	94.3 ± 3.4 a, b	2.5	88.9 ± 1.5 a
10%	95.0 ± 0.3 a	10.0	84.5 ± 2.0 b, c
20%	94.9 ± 3.0 a, b	20.0	81.8 ± 2.1 b, c
30%	92.1 ± 1.7 b	40.0	76.8 ± 1.7 d

^aValues for each conversion efficiency of metam sodium in each experiment followed by different letters are significantly different ($\alpha = 0.05$) by Tukey's mean separation test.

Table 3

Pseudo-first-order rate constants for MITC formation at different metam sodium application rates in Arlington sandy loam

Metam sodium application rate (mmol kg ⁻¹)	10 ² k (min ⁻¹)	t _{1/2} (min)	r ²
0.5	15.4 ± 1.16	4.5	0.970
2.5	7.69 ± 0.61	9.0	0.978
10.0	6.37 ± 1.21	10.9	0.881
20.0	5.39 ± 0.64	12.9	0.950
40.0	3.72 ± 0.45	18.6	0.956

The effect of the initial metam sodium application rate on its conversion efficiency was calculated based on soil extracts of MITC (Table 2). The conversion efficiency declined with increasing metam sodium application rate. For example, the conversion efficiency of metam sodium to MITC, which was 95% at 0.5 mmol kg⁻¹, decreased to 76.8% in the soil treated with 40 mmol kg⁻¹ of metam sodium. These results indicate that both the conversion rate and the fraction of metam sodium converted to MITC depend on the metam sodium application rate.

3.4. Conversion of metam sodium under different soil and atmospheric conditions

The effect of soil properties on the conversion of metam sodium (0.5 mmol kg⁻¹) to MITC was examined in six soils of differing composition and origin. High conversion efficiency of metam sodium (>92%) was observed in all soils (Table 1). No significant relationship between the conversion efficiency and any measured soil properties was observed. In addition, the conversion of metam sodium in all soils was very rapid and complete

within 0.5 h. These results suggest that the conversion of metam sodium to MITC was independent of the soil type studied.

The conversion of metam sodium (0.5 mmol kg⁻¹) investigated in Arlington sandy loam under initially anaerobic and aerobic soil atmospheres showed no statistical difference in the conversion efficiency (Table 1). These results further support that the primarily mechanism of metam sodium conversion in soil is a non-oxidative cleavage process, whereas metam sodium transformation in solution may involve an oxidative mechanism (Wales, 2000; Turner and Corden, 1963).

3.5. Column experiments

Following metam sodium application at a depth of 20 cm, MITC was rapidly volatilized from the soil surface, with the maximum flux (~1.9 mg min⁻¹ m⁻²) occurring at about 19 h (Fig. 3A). Thereafter, the volatilization flux of MITC gradually declined (Fig. 3A). A similar volatilization flux pattern was observed after the direct application of MITC at 20 cm of the soil column, which peaked (~2.4 mg min⁻¹ m⁻²) at approximately 19 h (Fig. 3A). The lack of a delay in MITC volatilization suggests that the decomposition of metam sodium (in Vapam) to MITC occurred very rapidly once the concentrated fumigant solution contacted the soil. However, the maximum MITC flux was ~20% higher for application of MITC compared to the maximum MITC flux from soil columns treated with metam sodium at an equivalent dosage, which might be attributable to less than 100% conversion efficiency of metam sodium.

Application of 150 mL (2.7 cm) of water to the soil surface just before metam sodium application (20 cm depth) substantially reduced the

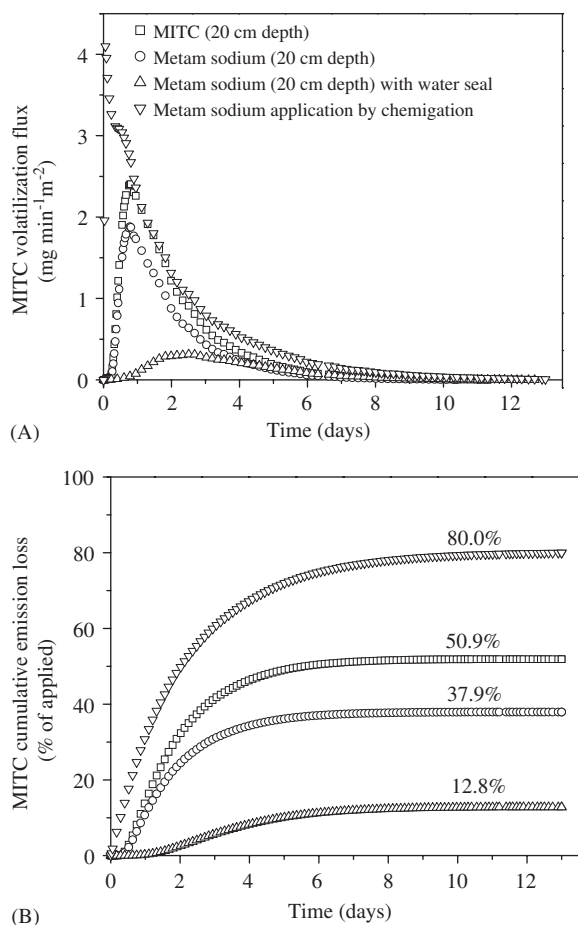


Fig. 3. Volatilization of MITC from soil with different application and surface treatments: (A) volatilization flux; and (B) cumulative emission loss.

volatilization flux of MITC and delayed the peak flux (Fig. 3A). The maximum flux of MITC from the water-sealed column was reduced by more than 80% relative to the soil column without any surface treatment when metam sodium was applied at 20 cm depth to both columns. The MITC flux in the water-sealed column showed a lag time of about 1 day before the volatilization flux increased, and maximum flux from the water-sealed column was delayed to 2.5 days after metam sodium application (Fig. 3A). These results indicate that the use of surface water sealing may be an efficient and economical method to reduce atmospheric emissions of MITC. Because of evapotranspiration at the soil surface, the emissions control provided by water sealing with a single application of water may be variable and will decrease with time. Applying water on an intermittent basis has been shown to be

a feasible method to minimize MITC emissions from fumigated fields (Sullivan et al., 2004).

In current fumigation methods, metam sodium is sometimes delivered by chemigation using sprinklers (Duniway, 2002). A column experiment was conducted to investigate the emission of MITC following simulated broadcast chemigation. Metam sodium solution (50 mL) was applied to the soil surface followed by 100 mL of water. An immediate flush of MITC occurred following the metam sodium chemigation (Fig. 3A). The maximum flux of MITC of $>4.0 \text{ mg min}^{-1} \text{ m}^{-2}$ occurred approximately 1–2 h after fumigation. Compared to the shank injection of metam sodium with a water seal, the surface chemigation application substantially increased MITC volatilization fluxes, although a similar amount of water was applied at the soil surface. The high concentrations of MITC in air that might result from this fumigation practice may pose a potential risk of acute pesticide poisoning to farm workers and others. This implies that an additional emissions reduction practice may be required to control MITC emissions when applying metam sodium by broadcast chemigation.

The cumulative emission losses occurring over 13 d from the soil columns with different treatments are shown in Fig. 3B. Most of the MITC loss occurred within the first 5 d. The total emission losses of MITC from columns with no surface treatment were 50.9% of the applied MITC (direct injection of MITC) and 37.9% (metam sodium application with equivalent theoretical MITC dosage). Surface water sealing significantly reduced the cumulative emission loss of MITC by approximately 66% relative to soil columns with no surface treatment and metam sodium injection at 20 cm (Fig. 3B). Also, a lag period (1–2 d) before the emission started to increase was evident for water-sealed columns with subsurface metam sodium application (Fig. 3B). These experiments indicate that surface water sealing can reduce MITC volatilization flux and cumulative emission loss when metam sodium is applied to the subsurface. Therefore, this fumigation strategy has great potential to mitigate the acute toxicity of fumigant (volatilization flux), while also moderating chronic toxicity (total emission loss). Previous studies have indicated that increasing soil water content can restrict diffusion and reduce fumigant emissions (Gan et al., 1996; Jin and Jury, 1995).

Soil column studies indicated that surface application of metam sodium combined with surface

water sealing may not be an appropriate management method to reduce MITC volatilization. Approximately 80% of the applied MITC was lost when metam sodium was delivered in water to the soil surface. Compared to subsurface applications (such as shank injection), broadcast chemigation would be expected to result in large volatilization losses of MITC. Field studies have indicated that surface application of metam sodium results in higher MITC concentrations in air than subsurface applications (Saeed et al., 2000). Increasing the depth of fumigant application will increase the residence time of fumigant in soil, which allows more time for biotic and abiotic degradation of MITC in soil, thus reducing MITC volatilization. Previous field and laboratory studies have shown that increasing the depth of application can decrease emissions of other fumigants (Yates et al., 2003). In these experiments, ~62% of the applied MITC (assuming 100% conversion of metam sodium) was degraded or remaining in soil columns 13 d after metam sodium

application at 20 cm depth. However, only 20% of the applied MITC was retained or degraded in soil when metam sodium was applied by broadcast chemigation combined with water sealing.

A successful fumigation requires adequate fumigant concentrations throughout the targeted soil profile to provide consistent pest control. The distribution of MITC in the gas phase of soil columns under various treatments is shown in Fig. 4 for several time intervals after metam sodium application. Methyl isothiocyanate diffused rapidly after injection at 20 cm depth (Fig. 4A). Similar distribution patterns of MITC were observed in soil columns treated with metam sodium at 20 cm depth (Fig. 4B), and the highest concentration of MITC was observed at the spiking depth (20 cm below the surface). The concentration of MITC at the spiking depth observed 6 h after metam-sodium application (Fig. 4B) was ~80% of the maximum MITC concentration in soil columns directly treated with MITC (Fig. 4A), which further verifies that metam

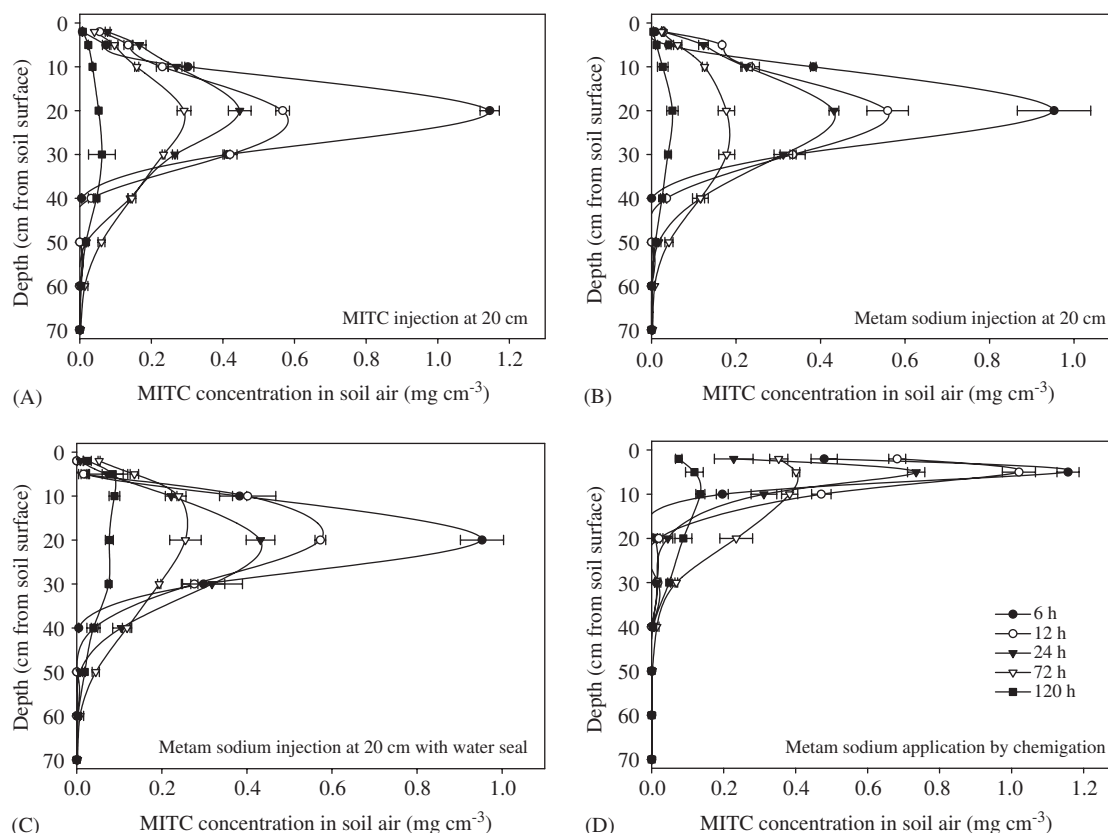


Fig. 4. Distribution of MITC in soil gas phase at different time intervals after fumigant application. (A) MITC application at 20 cm depth, no surface treatment; (B) metam sodium application at 20 cm depth, no surface treatment; (C) metam sodium application at 20 cm with surface water sealing; and (D) metam sodium application at the soil surface with water sealing.

sodium rapidly decomposes to MITC in soil with relatively high conversion efficiency.

Soil gas profiles in soil columns treated with metam sodium at 20 cm depth and a surface water seal (Fig. 4C) were similar to those in columns with no water seal (Fig. 4B) at times ≤ 24 h. After 24 h, MITC concentration profiles showed the impact of the diffusion barrier at the soil surface. Higher concentrations of MITC were observed in water-sealed columns than in columns with no water seal, especially at depths ≤ 30 cm. At 120 h, the concentration of MITC at each sampling depth was greater in water-sealed columns (Fig. 4C) than in soil columns without surface water application (Fig. 4B). The improved containment afforded by the water seal may provide an additional benefit in enhancing pest control efficacy while protecting air quality. Soil gas profiles in columns treated with metam sodium at the soil surface (Fig. 4D) exhibit a MITC distribution different from the subsurface applications (Fig. 4A–C). After metam sodium application at the soil surface by chemigation, the maximum MITC concentration occurred at the soil surface (< 5 cm) and subsurface (> 10 cm) concentrations of MITC were low throughout the monitoring period (Fig. 4D). These results suggest that an additional emission control method (such as tarping with a film) should be integrated with broadcast chemigation to reduce MITC emissions and enhance pest control efficacy.

4. Conclusion

The conversion of metam sodium to MITC occurs quite rapidly by an abiotic decomposition mechanism in soils. The effect of various soil factors on the rate and efficiency of conversion of metam sodium was determined at concentrations representative of typical field application rates. Complete conversion of metam sodium (0.5 mmol kg^{-1}) in all six soils tested in this study occurred within 0.5 h. The kinetics of metam sodium conversion to MITC was quantified from the evolution of MITC using a single exponential function. High conversion efficiency ($> 92\%$) was obtained in all soils when metam sodium was applied at typical field application rates (0.5 mmol kg^{-1}). The rate and extent of conversion decreased with increasing metam sodium application rate in soil.

Soil column experiments indicated that surface water sealing may reduce MITC volatilization in conjunction with subsurface application of metam

sodium, but may not be effective when metam sodium is surface applied. Water sealing did not reduce MITC concentrations in the soil gas, suggesting that water sealing may not adversely affect pest control. Because evapotranspiration reduces the effectiveness of a water seal with time, an intermittent water application may be required to control emissions, as has been demonstrated in field studies (Sullivan et al., 2004). While the soil column approach used in these experiments have been shown to accurately predict fumigant emissions under some conditions (Gan et al., 2000), it is difficult to replicate field conditions in the laboratory. The magnitude of emissions reduction and pest control (affected by subsurface MITC concentrations) achieved with water sealing will depend on prevailing soil and climatic conditions, and additional field research is needed to more completely evaluate this approach.

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